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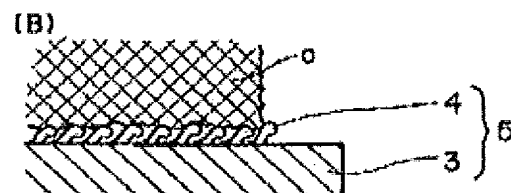
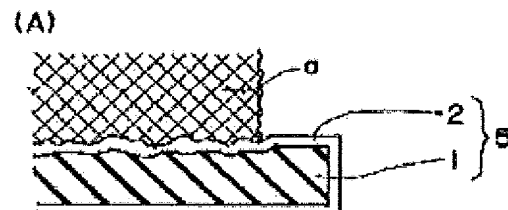
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(54) NONAQUEOUS SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a nonaqueous secondary battery of which electrical contact to the sintered body of a collector is good and stable.

SOLUTION: By using a collector 5 having an elastically deforming property, the collector 5 is tightly fitted to a positive electrode sintered body or negative electrode sintered body (a) and thereby, stable electrical contact can be maintained. For example, a member composed by covering an elastic body 1 with metal foil 2 or a conductive polymer 4 can be used as the collector.



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CLAIMS

[Claim(s)]

[Claim 1]A nonaqueous secondary battery the above-mentioned charge collector which laminates a charge collector, a cathode, an ionic conduction layer, and an anode at least, and it is a nonaqueous secondary battery to seal, and either [at least] the above-mentioned cathode or an anode is a sintered body, and touches this sintered body makes elastic deformation of the adhesion of possible to this sintered body.

[Claim 2]The nonaqueous secondary battery according to claim 1 with which the above-mentioned charge collector carries out the stratification of the conductive layer on the surface of an elastic base.

[Claim 3]The nonaqueous secondary battery according to claim 1 with which the above-mentioned charge collector carries out the stratification of the conductive polymer on the surface of a conductive base.

[Claim 4]The nonaqueous secondary battery according to claim 1 with which the above-mentioned charge collector comprises a conductive polymer.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to improvement of a charge collector in case either [at least] a cathode or an anode is a sintered body, concerning a nonaqueous secondary battery.

[0002]

[Description of the Prior Art]Although the high capacity lithium secondary battery attracts attention with the spread of a cellular phone, notebook computers, etc., the demand of space-saving square-shaped cells is increasing with a thin shape especially also in it.

[0003]However, into the electrode used for the present square-shaped cell, since what does not contribute to the capacity of an electrode originally [, such as a binder, a conducting material, and a metallic foil,] is contained, the cell capacity per volume is restricted. Since the portion of the buttock of a battery can cannot be filled up but a useless space will be made if the wound electrode is stored to a square-shaped battery can, the capacity per unit volume falls further.

[0004]Then, the trial which constitutes an electrode from a sintered body which consists of active materials substantially as one means to increase the capacity per unit volume is made. While being able to make pack density of an active material high and being able to increase the capacity per unit volume since a conducting material can be further reduced in needlessness or a small quantity excluding a binder if an electrode is constituted from a sintered body, the conductive improvement in an electrode is also expectable. For example, the anode which stuck copper foil to the sintered body of the petroleum pitch or the carbonaceous material by pressure, and the cathode which becomes JP,H8-180904,A from the sintered body of a lithium multiple oxide are indicated by JP,H5-299090,A. And the electrical link of the charge collector and sintered compact which constitute an electrode is secured by these sintered compacts' having a charge collector stuck by pressure, laminating them, being stored by the battery can, and pressurizing a battery can. [0005]

[Problem to be solved by the invention]However, when it depends for electric contact of a charge collector and a sintered body only on the press from a cell sheathing can, Since heavy-gage-ization of an armor can is needed for obtaining sufficient press, if the increase in battery weight is caused and press is insufficient on the other hand, Since an electric contact state changed with expansion contraction of the electrode accompanying charge and discharge, the problem on which the load characteristic and charging and discharging characteristic of a cell deteriorate, for example, capacity, fell, and there were a problem etc. to which discharge potential falls.

[0006]This invention aims at offer of the nonaqueous secondary battery in which the electric contact to the sintered body of a charge collector is good and stable.

[0007]

[Means for solving problem]To achieve the above objects, the charge collector which either [at least] a cathode or an anode is a sintered body, and touches this sintered body makes possible elastic deformation of the adhesion of the nonaqueous secondary battery of this invention to this sintered body.

[0008]Since a charge collector changes by this according to the minute unevenness on the surface of a sintered body, even if it is when the press from an armor can is small, good electric contact can be obtained. Change of the press by expansion contraction of the electrode at the time of charge and discharge is eased by the elasticity of a charge collector, and the stable electric contact can be obtained.

[0009]

[Mode for carrying out the invention]It explains referring to Drawings for the nonaqueous secondary battery of this invention. Drawing 1 is an outline sectional view showing an example of the nonaqueous secondary battery of this invention. The nonaqueous secondary battery of this invention laminates the charge collector 5, the cathode 6, the ionic conduction layer 8, and the anode 7 at least, and seals this to the battery armors 9, such as a stainless steel can. Although the cell when only the cathode 6 comprises a sintered body as an example was shown in the figure, it is accepted anode 7, or positive/negative two poles may comprise a sintered body, and the charge collector 5 and the same charge collector are used for all the sintered body electrodes in that case. The electric contact between each composition layer is maintained by the press from the battery armor 9.

[0010]Although any material publicly known as positive active material of a rechargeable lithium-ion battery can be used for the positive active material used for this invention, It is preferred to use lithium transition metal oxides, such as LiCoO_2 which doped LiCoO_2 , LiNiO_2 , LiMn_2O_4 of Spinel structure, and Mg.

[0011]When using the cathode constituted from a sintered compact, (This cathode is abbreviated to a cathode sintered compact), The powder mixture containing Li compound which turns into an oxide by heat treatment, and a transition metal

compound is fabricated at 500-900 °C to prescribed shape after temporary quenching under atmospheric air for about 0.1 to 10 hours, and is calcinated at 700-1100 °C under atmospheric air for about 0.5 to 24 hours. Here, Li and hydroxide of a transition metal, an oxide, a nitrate, carbonate, etc. are mentioned what serves as an oxide by heat treatment.

[0012]As negative electrode active material used for this invention, any material publicly known as negative electrode active material of a rechargeable lithium-ion battery can be used. For example, metal, such as aluminum which can form carbon materials, such as natural graphite, corks, and glassy carbon, silicon material, metal lithium and metal lithium, and an alloy, etc. can be mentioned.

[0013]the material which sintered (this anode is abbreviated to an anode sintered compact), a carbon material, silicon, and the material heat-treated and carbonized as a raw material when an anode was constituted from a sintered compact -- a simple substance -- or it can compound and can use as an anode. As a material heat-treated and carbonized, phenol resin, an epoxy resin, Unsaturated polyester resin, furan resin, urea resin, melamine resin, an alkyd resin, Thermosetting resin, such as xylene resin, naphthalene, an acenaphthylene, phenanthrene, The pitch etc. which use condensed system polycyclic hydrocarbon compounds, such as anthracene, triphenylene, pyrene, a chrysene, a naphthacene, picene, perylene, penta Foehn, and pentacene, the derivative of those, or these mixtures as the main ingredients are mentioned.

[0014]While the charge collector 5 has electron conductivity, it needs to make elastic deformation of the adhesion possible to a cathode sintered body or an anode sintered body. The fragmentary sectional view of the contacting parts of the charge collector 5, a cathode sintered body, or the anode sintered body a (it abbreviates to the sintered body a hereafter) is shown in drawing 2 (A). As typically shown in drawing 2 (A), the charge collector 5 can be stuck to the sintered body a surface which has minute unevenness on the surface by carrying out elastic deformation, and the press change from the exterior by expansion contraction of an anode and a cathode can be eased, and the stable electric contact between the sintered bodies a can be obtained.

[0015]This charge collector 5 can be constituted by, for example, carrying out the stratification of the conductive layer 2 to the surface of the elastic base 1, as shown in drawing 1 and drawing 2 (A). In the elastic base 1, for example Isobutylene isoprene rubber, ethylene-propylene rubber, Thermoplastic elastomer, such as various vulcanization mold rubbers, such as urethane rubber, polysulfide rubber, and fluorocarbon rubber, or a polystyrene system, a polyolefin system, a polyurethane system, a polyester system, a polyamide system, polyvinyl chloride, and a polyfluorocarbon system, can be used. Especially, use of adhesion with an electrode and the viewpoint of an electrolysis solution-proof to a polyolefin elastomer is preferred. When using the charge collector 5 for a cathode sintered body, aluminum, titanium, platinum, the alloy containing these, or conductive carbon can be used for the conductive layer 2. When using for an anode sintered body, copper, nickel, a platinum metal, or the alloy containing these can be used for the conductive layer 2. Although the thinner one of the thickness of the conductive layer 2 is advantageous from a viewpoint of the adhesion to the sintered body a, since intensity runs short if too thin, it is 10-100 micrometers more preferably 1-500 micrometers. the field where the conductive layer 2 touches the sintered body a of the elastic base 1 surface at least -- a wrap -- it needs -- it is preferred to carry out the stratification -- attachment of a metallic foil -- or it can twist and the stratification can be carried out by spreading of metal paste or conductive carbon paste, etc.

[0016]A charge collector may be constituted by carrying out the stratification of the conductive polymer 4 to the surface of the conductive base 3, as shown in drawing 2 (B). In this case, elastic deformation nature required for the charge collector 5 is obtained with the elasticity which the conductive polymer 4 has. The conductive base 3 plays the role which assists the electronic conduction of the conductive polymer 4 simultaneously when it comes to the base material of the conductive polymer 4. When using the charge collector 5 for a cathode sintered body, an aluminum plate, a titanium plate, a platinum board, a stainless plate, the alloy plate containing these, or a conductive carbon board can be used for the conductive base 3, for example. Especially, use of the viewpoint of weight, thinness, and economical efficiency to an aluminum plate is preferred. When using the charge collector 5 for an anode sintered body, a copper plate, a platinum board, a nickel board, a stainless plate, or the alloy plate containing these can be used for the conductive base 3, for example. Especially, use of the viewpoint of economical efficiency and endurance to a copper plate is preferred. In the conductive polymer 4, they are polyacetylene, Poly p-phenylene, poly aniline, polypyrrole, a polythiophene, a polyindole, polycarbazole, a polyazulene, poly acene, etc., for example. The viewpoint of high electron conductivity to polypyrrole is especially preferred. As for the thickness of the conductive polymer 4, it is more preferably preferred from the viewpoint of elastic deformation nature and electron conductive reservation that it is 1-100 micrometers 1-1000 micrometers. The stratification to the surface of the conductive base of the conductive polymer 4 may be performed by sticking or twisting the compound conductive polymer film around a conductive base, and may be performed by carrying out electrolytic polymerization of the conductive polymer 4 directly on the conductive base 3.

[0017]A conductive polymer independent may constitute a charge collector. In this case, a conductive polymer is provided with both elastic deformation nature required as a charge collector, and electron conductivity. The stratification of the conductive polymer may be carried out on a suitable base material, and it may also be included in a cell, may be formed in a thick film and may also be independently included in a cell. A conductive polymer may be directly formed at the rear face of a sintered body. It is electrochemically and chemically stable within a cell, and the above-mentioned base material has a mechanical strength which is equal to the press from the exterior, and should be just usable in various materials, such as a resin sheet and a ceramic plate.

[0018]Its all are usable if the ionic conduction layer in the nonaqueous secondary battery of this invention is a nonaqueous electrolyte generally used for a nonaqueous secondary battery. For example, the solid polymer electrolyte which made the nonaqueous electrolyte made to dissolve lithium compounds, such as lithium hexafluorophosphate, in the organic solvent of a carbonate system or the organic solvent in which dissolution or a lithium compound was dissolved for the lithium compound hold can be used.

[0019]

[Working example] Three polyolefin sheets (parafilm) working-example 1 (production of charge collector) 100 micrometers in thickness, and 22 mm in diameter were laminated, this was wrapped in 14-micrometer-thick aluminium foil, and this was made into the charge collector.

[0020] (Production of a cathode) Lithium carbonate powders and cobalt carbonate powder were mixed so that it might become the mole ratio 1:1, and temporary calcination was carried out at 800 °C among atmospheric air for 5 hours. Subsequently, this was ground, it mixed 5 weight %, pressing of the spherical polymethylmethacrylate particle with a mean particle diameter of 5 micrometers was carried out, it calcinated at 900 °C among atmospheric air for 10 hours, and the sintered body of 20 mm in diameter, 0.3 mm in thickness, and specific gravity [of 3.0 g/cm³] was obtained.

[0021] (Production of an anode) Crystalline substance silicon powder 80 with the purity of 99.9%, and a mean particle diameter of 1 micrometer weight section, and graphite / pitch mixture 20 weight section, It mixed with n-methyl-2-pyrrolidone solution (11.8 weight %) 170 weight section of polyvinylidene fluoride, and was considered as paste state, and the part was dried after applying to copper foil. This was started to a disk type 20 mm in diameter, it calcinated at 1100 °C under a nitrogen atmosphere for 3 hours, and the anode of 0.22-mm [in thickness] and specific gravity 1.2 g/cm³ was obtained.

[0022] (Production of a coin type cell) The charge collector, the cathode, the polyethylene porous membrane as an ionic conduction layer, and the anode which were obtained were laminated, it stored to the armor can made from stainless steel, and the coin type cell was produced. What carried out 1 mol/L dissolution of the lithium hexafluorophosphate was used for the electrolysis solution at the mixed solvent (volume ratio 1:1) of ethylene carbonate and dimethyl carbonate.

[0023] (Evaluation of a coin type cell) the result of having done the constant current fixed voltage charge and discharge test in the current rate 0.3C -- average discharge potential -- about -- 100mAh and the charge and discharge efficiency of 3.4V and service capacity were 100% per cathode weight.

[0024] Production of a cell and evaluation were performed by the same method as the working example 1 except production of working-example 2 charge collector. Prepare a stainless plate 300 micrometers in thickness, and 22 mm in diameter, and electrolytic oxidation polymerization is performed by making this into an electrode for 2 hours into the acetonitrile fluid (0.05 mol/L) of tetraethylammonium p-toluene sulfonate, The polypyrrole film was formed 10 micrometers in thickness on the above-mentioned stainless steel board. When the stainless plate with which this polypyrrole film was formed was used as the charge collector, as for average discharge potential, 100mAh and the charge and discharge efficiency of about 3.4 v and service capacity were 100% per cathode weight.

[0025] Production of a cell and evaluation were performed by the same method as the working example 1 except production of a comparative example charge collector. When aluminium foil (22 mm in diameter and 14 micrometers in thickness) was used as the charge collector, as for average discharge potential, 70mAh and the charge and discharge efficiency of 3.2V and service capacity were 98% per cathode weight.

[0026]

[Effect of the Invention] Since the nonaqueous secondary battery of this invention has [a charge collector] elastic deformation nature, even if it is when the press from a battery armor is small, a charge collector can stick it to a sintered body, and it can contact electrically good. Since the elastic deformation nature which a charge collector has eases change of the press by expansion contraction of the electrode at the time of charge and discharge, the stable electric contact is maintainable.

[Translation done.]